AEROSOL MANUFACTURING TECHNOLOGY FOR PRODUCTION OF LOW-COBALT LI-ION BATTERY CATHODES

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Project ID# bat411

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OVERVIEW

Timeline

- Project start date: 10/01/2018
- Project end date: 12/31/2021
- Percent complete: 40%

Budget

- Total project funding: $3,749,057
  - DOE share: $2,989,057
  - Contractor share: $ 760,000
- Funding for BP1 (2018-19): $1,133,905
- Funding for BP2 (2020): $1,369,863
- Funding for BP3 (2021): $1,245,289

Barriers and Technical Targets

- Performance: cell chemistries that provide higher energy have life and performance issues
- Life: next-gen technologies still suffer major cycle and calendar life issues.
- Cost: main drivers are the high cost of raw materials and materials processing, the cost of cell and module packaging, and manufacturing costs

Partners

- ANL: Joseph Libera – Flame Spray Pyrolysis development, Eungje Lee- cathode development
- SAFT: Joong Sun Park, Carine Margez – cell fabrication and testing

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RELEVANCE - PROJECT OBJECTIVES

Impact:

- Address both cost and performance challenges for the next-generation Li-ion batteries (LIB). If successful, the project will have significant impact on cost reduction of Li-ion battery towards the $100/kWh target
- Flexibility to produce all key Low-Cobalt cathode compositions

Objective:

Research, develop, and demonstrate Reactive Spray Technology (RST) and Flame Spray Pyrolysis (FSP) for production of low-Cobalt active cathode materials for use in next-generation Li-ion batteries (LIB) capable of achieving the following performance targets:

Beginning of Life Characteristics at 30°C	Cell Level	Cathode Level
Useable Specific Energy @ C/3		≥600 Wh/kg
Calendar Life (< energy fade)	15 Years	
Cycle Life (C/3 deep discharge <20% energy fade)	1,000	
Cobalt Loading	≤ 50mg/Wh	
Cost	≤ $100/kWh	

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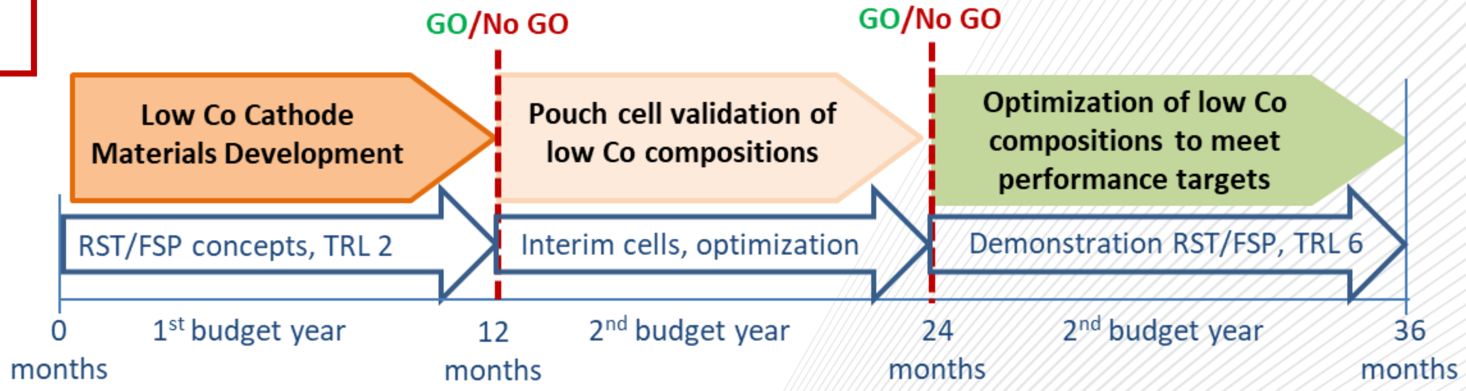
APPROACH/STRATEGY

How to enable low/free Cobalt cathodes and improve cost and performance?

1. Materials supply chain optimization
   - Access to metals, strategic collaborations
2. Materials Improvements
   - Compositional modifications (less Co, cheaper raw materials)
   - Surface modifications (coatings, core/shell)
3. Improved synthesis process
   - Often as important as composition
   - Industry needs new ideas and approaches

Approach

- Develop Low-Cobalt cathode materials via Reactive Spray Technology (RST) and Flame Spray Pyrolysis (FSP) targeting < 50 mg_{Co}/Wh
- Implement structural and morphological modifications through aerosol particle production process
- Synthesize high Ni content NCM and disordered rock-salt materials
- Optimize conductive additive formulations for Low/free Co active material



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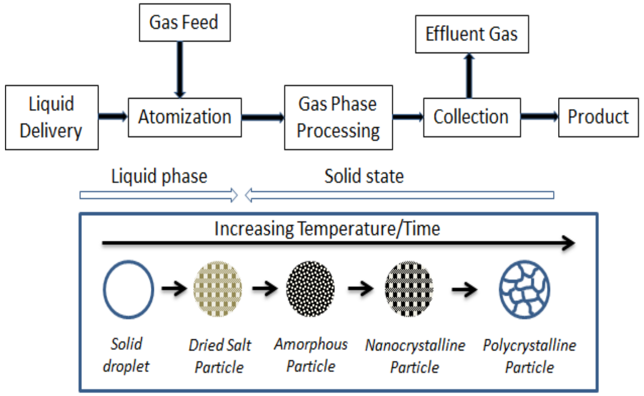
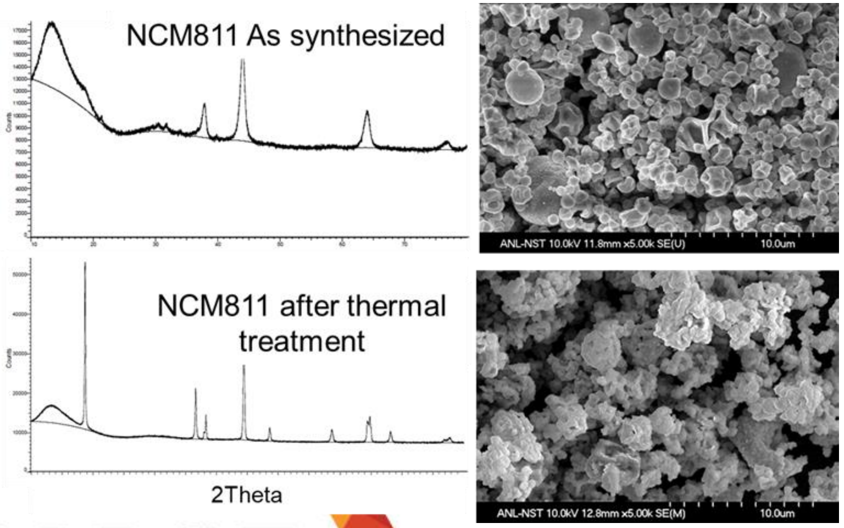
SYNTHESIS AND OPTIMIZATION OF CAMs BY RST

Reactive Spray Technology (RST) System

- Continuous process eliminates/simplifies heat treatment
- Fine spray/dry feed for small and controllable particle size
- Liquid precursors enables compositional flexibility and homogeneity: control particle density (chemical/physical)

RST system at Argonne National Lab (MERF)





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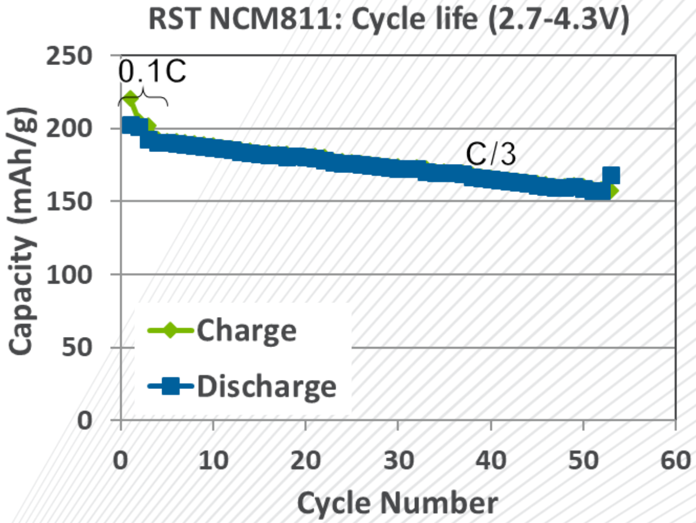
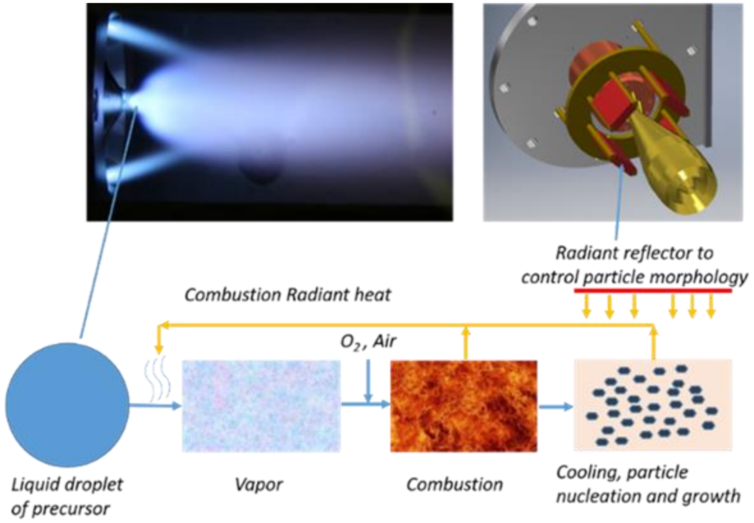
- NCMs (622, 811, 9055) have been produced
- Layered structure is obtained after annealing at temperatures above 750°C
- NCM811 half cell (0.1C, 2.7-4.3V), 1st discharge: 202 mAh/g capacity with 91% C.E.
- Performance: 120 cycle at 80% retention (not optimized particle)

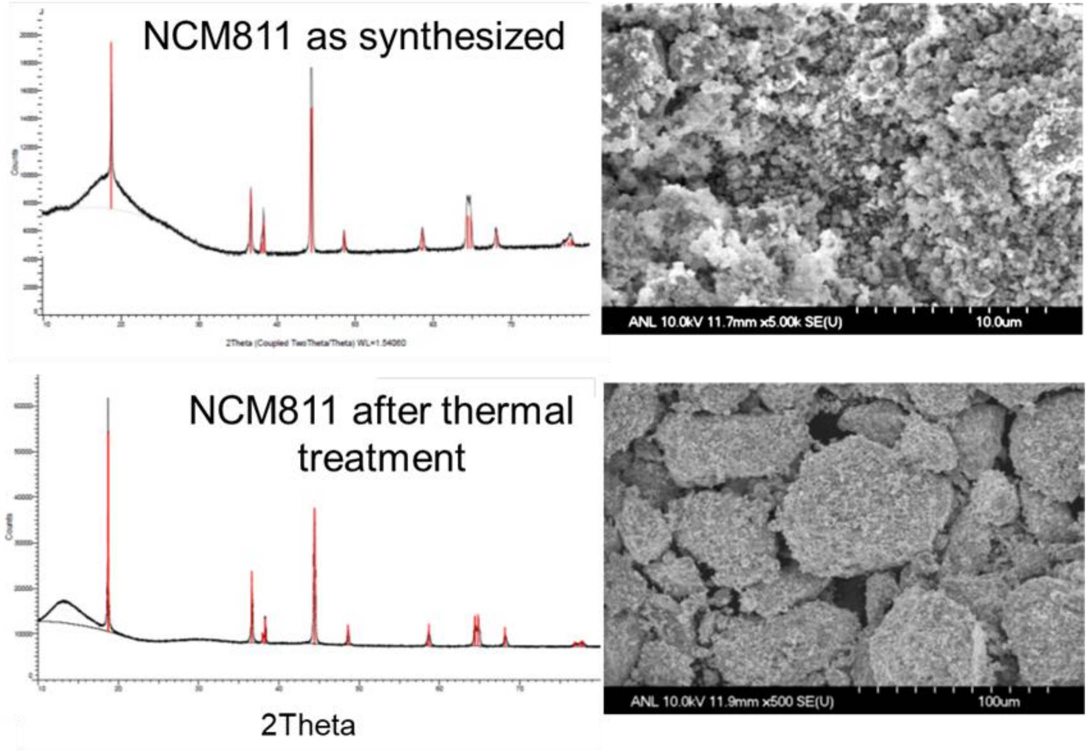


SYNTHESIS AND OPTIMIZATION OF CAMs BY FSP

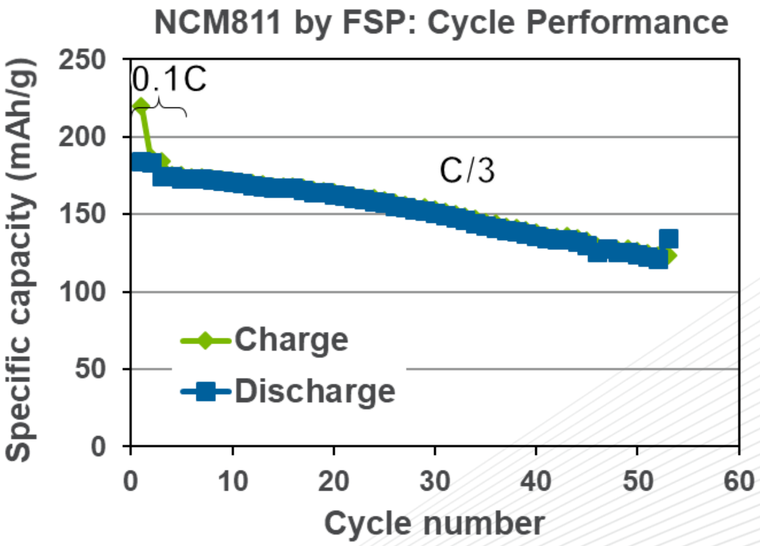
Flame Spray Pyrolysis (FSP) System

- FSP is a subtype of aerosol synthesis techniques
- Aerosol manufacturing processes for high-volume continuous manufacturing of battery cathode powders and solid-state electrolyte
- ANL has built and commissioned an FSP system optimized for battery materials synthesis



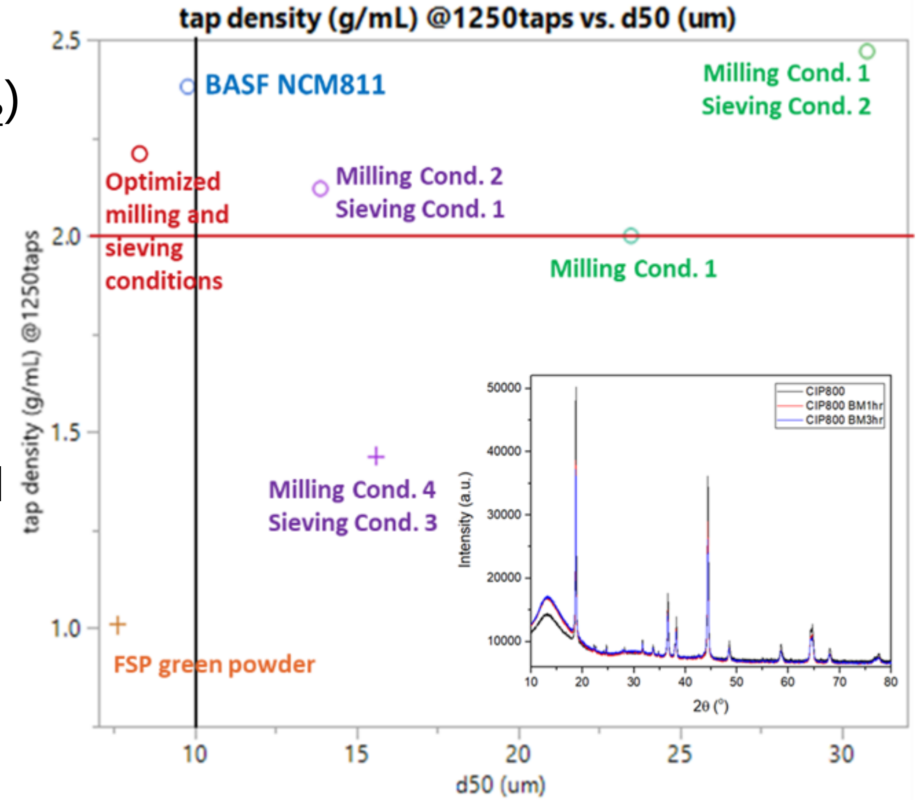


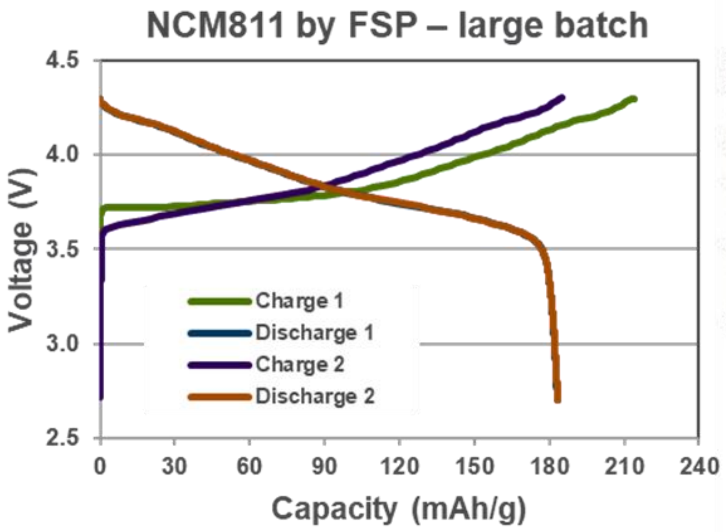
- As-prepared NCM primary particles 20 - 200 nm
- Initial disordered rock salt type transforms to layered structure after thermal treatment
- NCM811 half cell (0.1C, 2.7-4.3) 1st discharge capacity : 186 mAh/g with 86% C.E.
- Performance: 80 cycles at 80% retention (not optimized particle)

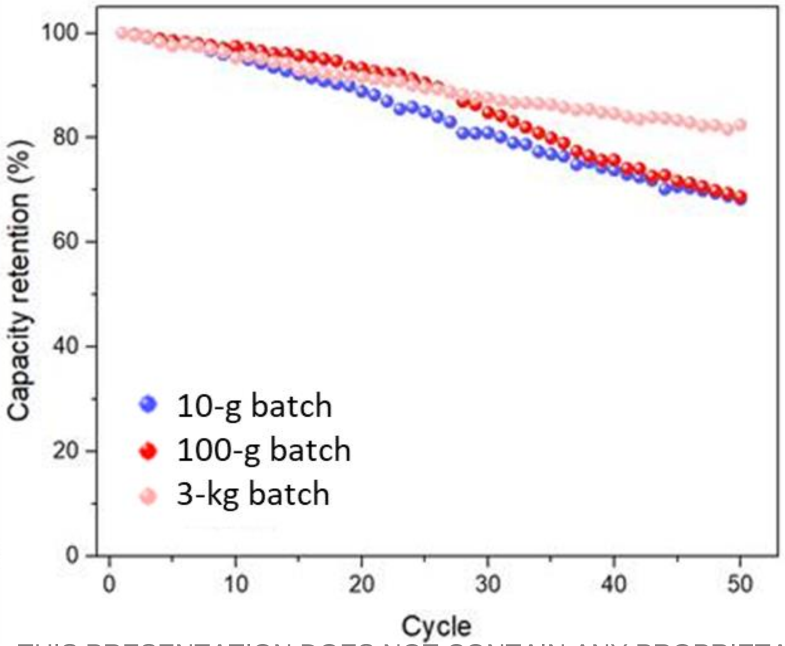


SYNTHESIS AND OPTIMIZATION OF NCM811: SCALE UP

- PPC synthesis campaign: water-based nitrate precursor (RST and FSP), 50 to 100-g batches, annealing 100-200g per batch (under O_2)
- Post-processing:
  - Milling/sieving: dry and wet to control particle size and tap density
  - Washing with water/alcohol to remove surface contaminants
- Physical properties: Tap density: 2.0-2.2 g/cm^3 and D50: 4-6μm
- Crystallite size decreases as milling energy increases, further experiments on-going to understand implications on electrochemical performance





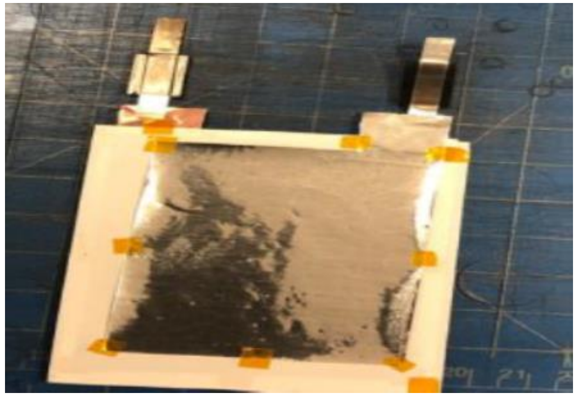


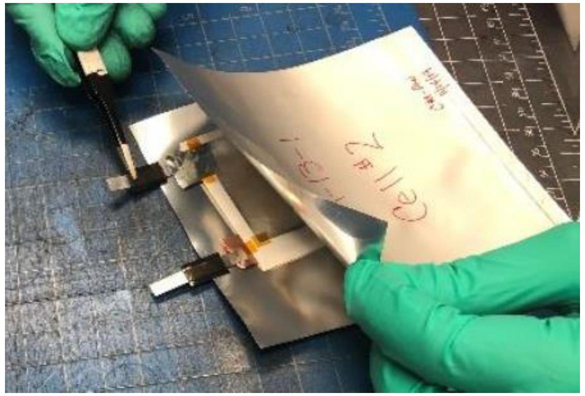
- Half coin cells were built with scaled up NCM811:
  - Two formation cycles at @ 0.1C (CCCV)
  - Cycling at @ 0.33C between 2.7 and 4.3V
- Similar electrochemical performance between small and larger scales

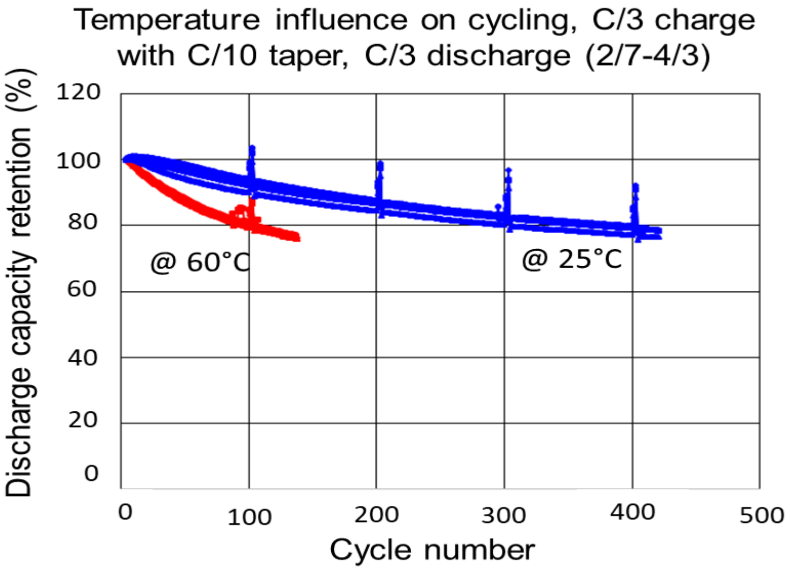
OTHER CELL COMPONENTS AND POUCH CELL TESTING

Other cell components

- SAFT made/tested >30 pouch cells with different formulations to qualify other cell components for project progress cells (PPCs)
- Cells were tested for: cycle life at 60°C, cycle life at 25°C and calendar life at 60°C
- Cell components were selected: natural graphite, electrolyte, binder and conductive additive (LTXHP, Cabot R&D product).







Pouch cell testing

- Double layer pouch cells (150mAh) were made with NCM811 made by FSP and RST
- The NCM811 cathode electrodes were matched with graphite anodes (balanced N/P= 1.2)
- Cells were filled with SAFT selected electrolyte, cycle life was performed at C/3 rate, 2.7-4.3 V, at 25 and 60°C
- Cells have cycle for over 300 cycles at 80% capacity retention

COLLABORATIONS

- Argonne National Laboratory (ANL): Cathode compositions, cathode synthesis (FSP and RST), synthesis know-how, battery and analytical capabilities
  - ANL team has been working on Li-ion cathodes and other battery materials for more than 15 years. They have extensive understanding of cathode materials, electrodes, and unique facilities for the fabrication, characterization and testing of battery materials.
  - ANL team has developed high performance LIB cathode compositions such as layered-layered high energy materials with extremely high capacity.
- SAFT: Battery design, fabrication and testing; will assist selecting battery component materials
  - World leader in providing Li-ion systems for commercial, defense and space markets.
  - Experience manufacturing pouch cells ranging from 2Ah to 50Ah.
- STA Technologies/SICPA: collaboration to scale up RST and FSP production of powders

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STA Technologies, LLC

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PROPOSED FUTURE WORK

Remainder of BP2 (2020)

- Complete production of NCM811 by RST to fabricate PPCs and delivered them to DOE and TARDEC
- Continue improving cathode compositions with initial focus on $Li(Ni_{1-x-y}Co_xMn_y)O_2$ (x, y ≤1) and then Li-excess disordered rock salt (LxDRS)
- Surface coating/modification of the Low-Co CAM to improve cycle life and CAM slurry processability
- Continue cell components selection and formulation optimization: conductive additive formulations, cathode slurry and coating process trials and optimization, and formation procedure
- Assemble pouch cells using improved low-Co compositions (≥ 200mAh): optimizations in mixing, coating, calendaring, stacking, filling, and formation procedure
- Any proposed future work is subject to change based on funding levels

Go/No Go (12/2020): Pouch cell validation of low-Co compositions:

- Fabrication and testing of Interim pouch cells
- Cell performance: 600 Wh/kg (cathode) and 80% SoC after 300 cycles

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SUMMARY

Relevance

- Address cell cost (≤ $100/kWh) and cathode performance (≥ 600Wh/kg) challenges for the next generation LIBs
- Flexibility to produce all key low-Cobalt cathode compositions

Approach

- Develop low-Co cathode materials via RST and FSP targeting < 50 mg_{Co}/Wh
- Implement structural/morphological modifications through aerosol particle production process
- Synthesize high Ni content NCM and disordered rock-salt materials
- Optimize conductive additive formulations for Low/free Co active material

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Technical Accomplishments

- RST and FSP systems optimized to produce low-Co CAMs
- NCM 811 and 9055 were made with FSP and RST
- RTS made CAMs show better particle tuneability, higher specific capacity improved performance compared to FSP
- Water wash/alcohol milling has been used to remove surface contaminants and improve processability and life performance
- Surface coating using nano NCM111 (by FSP) on NCM811 have shown to improving cycle life

Future Work

BP2 (2020)

- Synthesis and optimization of RST/FSP low-Co cathode materials to improve cell energy and cycle life
- Cell components selection and formulation optimization
- Fabrication and testing of Interim pouch cells

BP3 (2021)

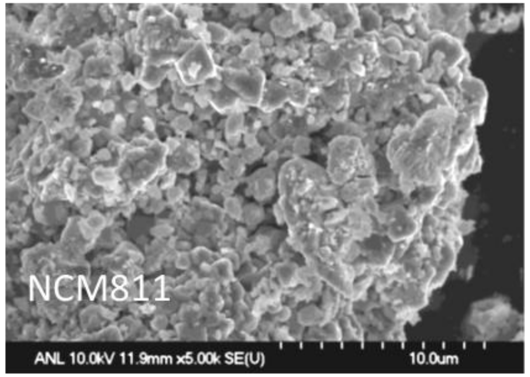
- Optimization of low-Co compositions to meet performance targets
- Project Completion Cells (PCC, ≥2Ah) build and test

TECHNICAL BACK-UP SLIDES

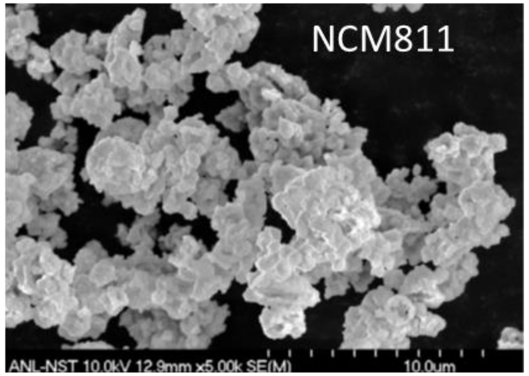
SYNTHESIS AND OPTIMIZATION OF CAMs: RST vs. FSP

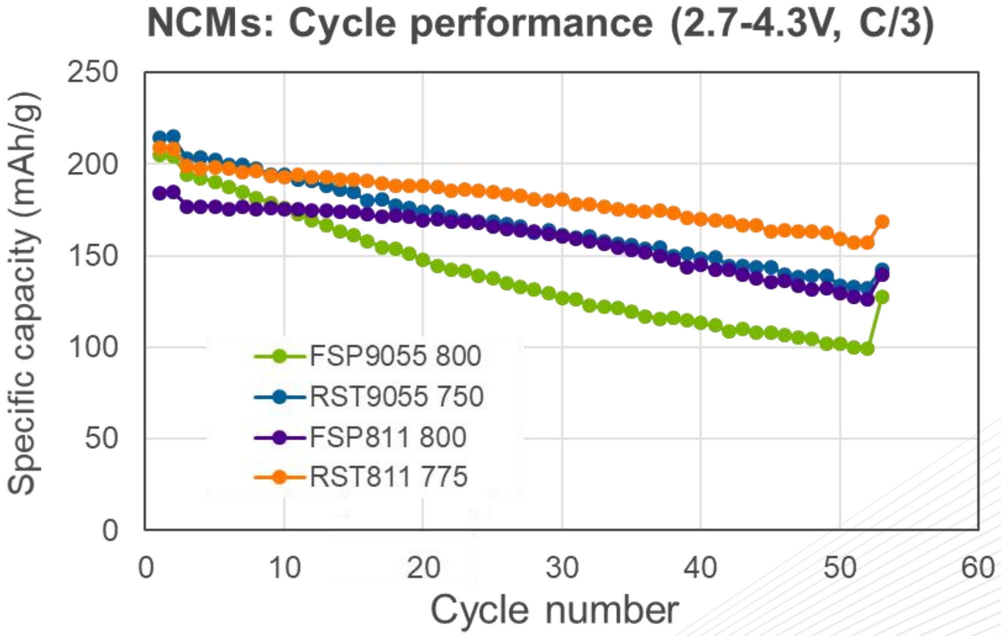
- RST: micron-size particles (containing nano-domains), broader range of particle synthesis
- FSP: higher reactor temp. and shorter reactor time, nano-sized particles with variety of morphologies
- Same material targets using both systems: greater fundamental understanding of material outcomes
- NCMs made by both technologies: same chemical composition, different particle morphology and electrochemical performance
- Half coin cell data shows advantages (initial capacity, C.E. and cycle life) of the CAMs made by RST over FSP
- The nature of the RST system allows the usage of higher precursor loading, which means higher throughput
- CAMs synthesis moving forward: RST larger batches for cell deliverables, FSP nano particles for surface modification

FSP, after thermal treatment



RST, after thermal treatment



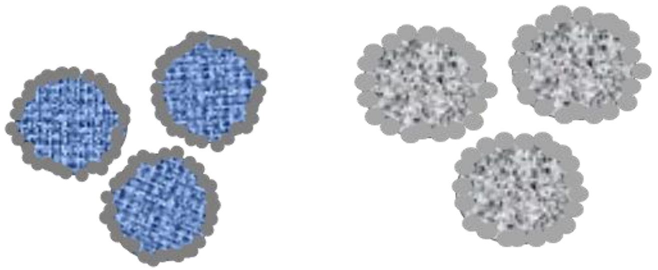


ACTIVE MATERIAL SURFACE MODIFICATION STUDIES

Cathode active material surface coating:

- Barrier between the cathode material and the electrolyte: side reactions mitigating to improve long term cycle life
- Shown to be effective preventing undesired changes at the surface of the particle

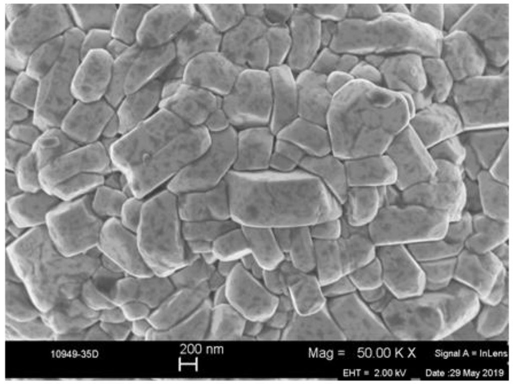
Dry coating: Coating of secondary particle and some M-doping

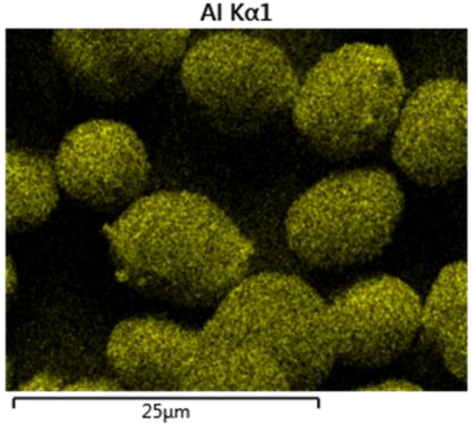


MO_x/NCM811

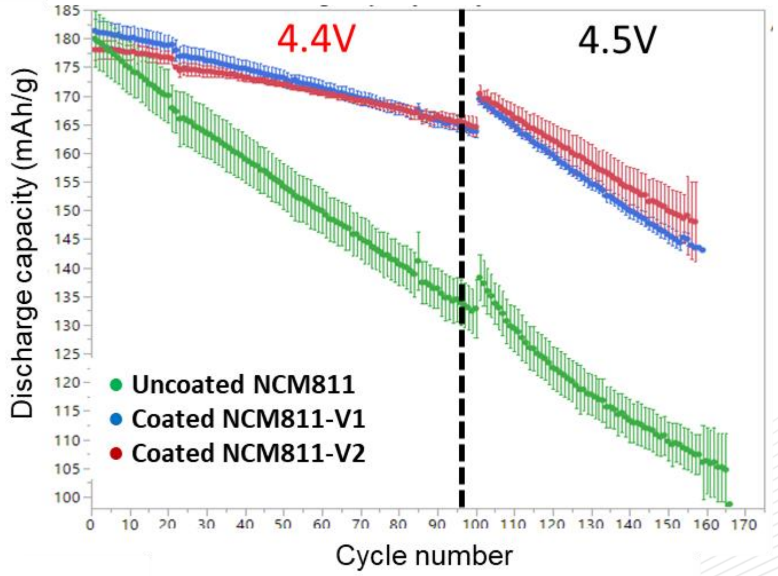
Gradient like NCM111/NCM811

Al_2O_3 dispersed on NCM811 after thermal treatment





Full cell cycling under high voltage at 45°C, 1C/1C



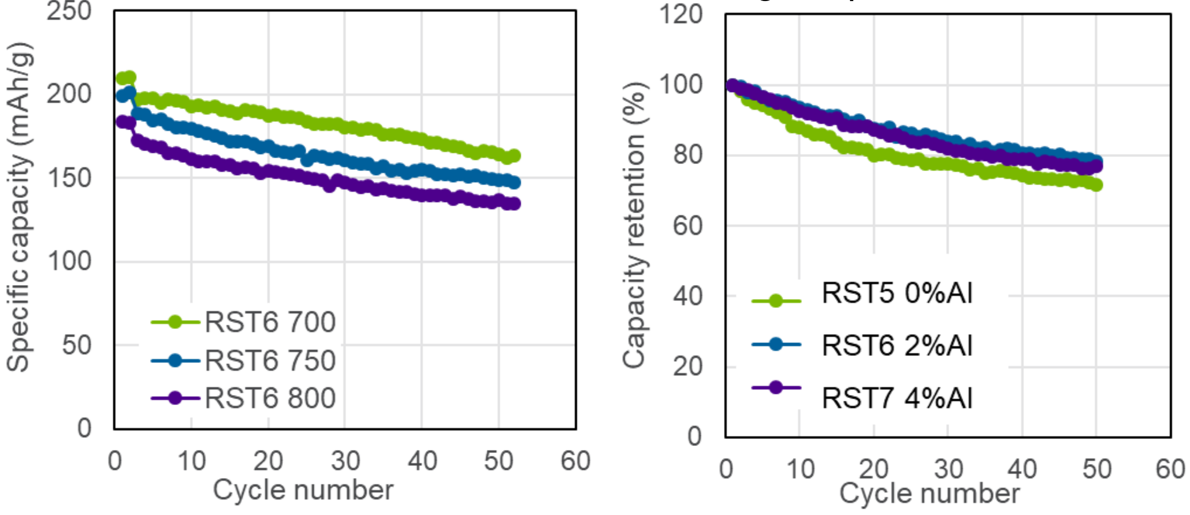
Dry coating

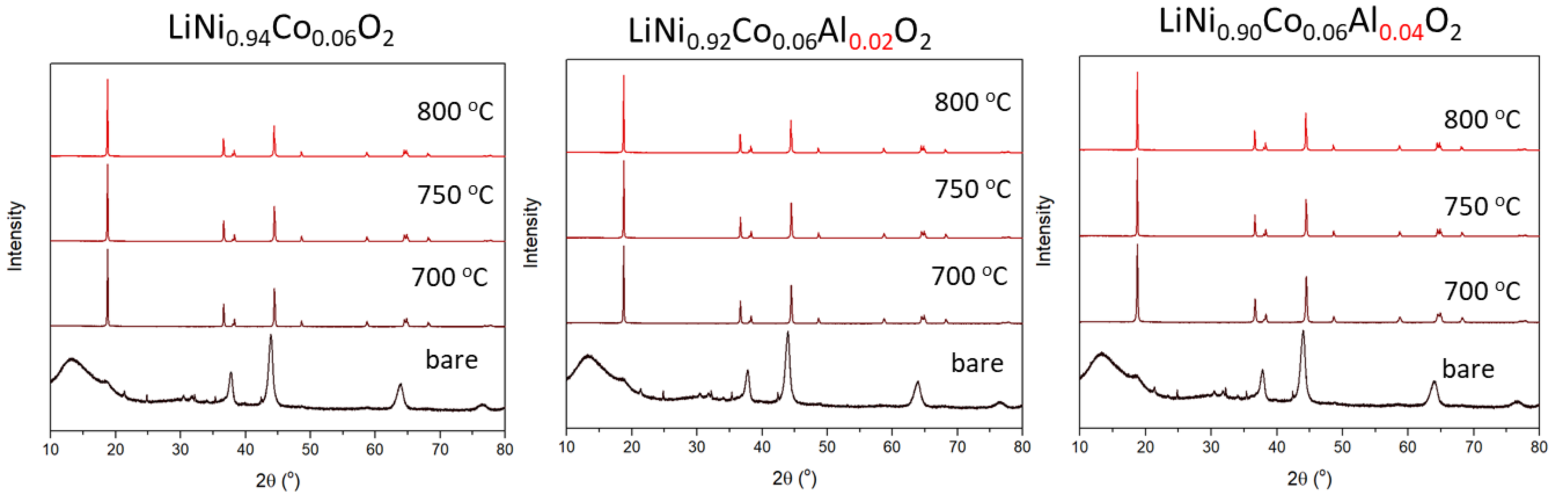
- Use custom design nanoparticle (FSP): metal oxide, including fumed oxides, Li-metal oxides and Li-ion active materials
- Enables gradient structures: to improve the performance and safety of the battery
- Encouraging initial results using both MO_x and nano-NCM111 as surface coating precursors

SYNTHESIS OF LOWER COBALT CAMs

- Co loading requirement, < 50mg$_{Co}$/Wh: composition needs to be optimized to reduce Co content and/or enhance energy density
- Candidates to move onto the lower-Co target: $LiNi_{0.9}Co_{0.05}Mn_{0.05}$ and $Ni_{0.9-x}Co_{0.06}Al_x$ x=0.005-0.03
- NCM9055 has been developed by RST and FSP showing high capacity, however the cycle life performance is sacrificed
- NCA with reduced amounts of Co have ben produced by RST

NCA electrode half cells: different annealing temperature and Al wt.%





NCA by RST :

- High temperature anneal leads to lower capacity due to sub-stoichiometric Li and more Li/Ni mixing
- 2% Al doping seems to be the most promising candidate based on capacity and cycle performance results